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**Free-Electron-Laser Spectroscopy of
Semiconductor Surfaces and Interfaces**

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The inauguration and long-term successful operation of the Vanderbilt Free-Electron Laser (FEL) has opened up extraordinary opportunities for semiconductor research. The Vanderbilt FEL is continuously tunable over a broad spectral range; this range, easily augmented by frequency multiplication and higher-harmonic operation, covers the band gaps of most of the technologically important semiconductors. The FEL's high average power and peculiar time structure has been exploited in a number of advanced semiconductor spectroscopies that promises to increase our understanding of the electronic structure and dynamic response of these fundamentally interesting and technologically crucial materials.

Our program is built on a firm and concrete background, with a record of results that has fulfilled the initial promise involving the systematic use of an FEL in semiconductor and materials research. Significant results have been obtained in a number of areas but we will emphasize to special topics: (a) FEL Internal Photoemission (FELIPE) measurements of interface energy barriers, and (b) two-photon absorption in germanium. In the case of FELIPE, the first results, which were also the first FEL data on surfaces or interfaces, concerned heterojunction band discontinuities. This has been for many years a central problem in solid state science, with fundamental and applied aspects. The research had

reached a major roadblock, since the test of theories required an accuracy much better than 10 meV, and the standard measurements were either not sufficiently accurate or not sufficiently reliable. The FELIPE idea is very simple and straightforward: the FEL is used to excite carriers across the barrier to be measured, thereby enabling them to produce a photocurrent in an external circuit. The first measurements immediately reached the best levels of accuracy and reliability, and subsequent improvements (Fig. 1) have brought the accuracy to a very few meV.

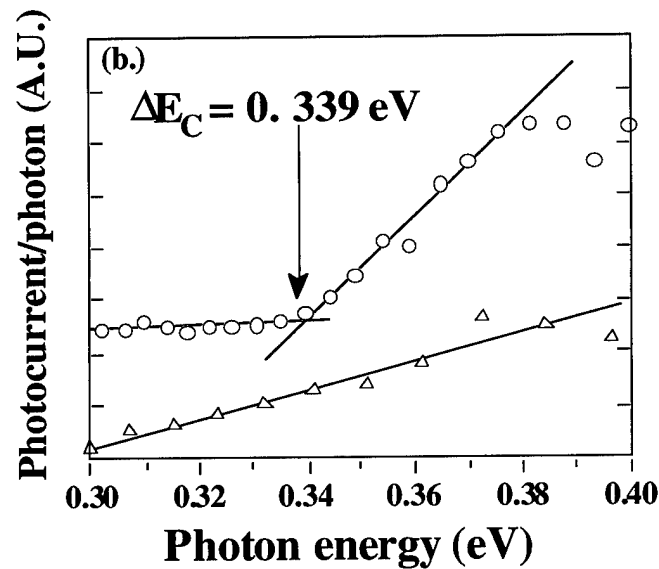


Fig. 1. Typical FELIPE photocurrent measurement of a GaAs/a-Ge interface at 77 K with a +0.8 V bias applied to the GaAs side. A simple linear fit to the threshold region determines the discontinuity. The bulk photoconductivity of the GaAs was measured to verify that the FELIPE threshold was not due to a bulk GaAs impurity band.

FELIPE is now an almost routine technique, that has been successfully used for a number of interfaces, notably in the GaAs-AlGaAs and GaAs-Ge family. Cross tests with conventional sources enhance the reliability and add information on other parameters such as the local forbidden gap. It should be emphasized, however, that the straightforward character of the technique is made possible by the use of the FEL, which provides the right tuning range for the photon energy so that barriers can be measured directly rather than derived indirectly. This is a major point in the superiority of FELIPE. Other relevant points are that FELIPE can be applied to *buried* interfaces rather than being confined to thin overlayers as are the standard photoemission measurements. The present status leaves

ample possibilities of further improvements of the technique, for example the achievement of high lateral resolution. It should be noted, however, that even without considering further improvements, the technique is already the premier available approach for the measurement of energy barriers at semiconductor interfaces.

The second series of concrete results concerns the nonlinear optical properties of the elemental semiconductor germanium. This research is a byproduct of a major effort for the study of nonlinear optical absorption of artificial semiconductor microstructures. While assessing the best strategy, we realized that there still existed major gaps in the knowledge of the two-photon absorption of some of the basic semiconductors that are used to form artificial structures. Germanium was the most striking case: probably because of the indirect nature of its gap and of the subsequent weakness of the two-photon absorption, no attempt had been made in over eighteen years to study such an absorption. We then decided to use the superior properties of the Vanderbilt FEL and try to eliminate this fundamental missing point in our knowledge of a basic material such as Ge. This attempt was rewarded by an unqualified success. The data (Fig. 2) clearly exhibited both the direct and the indirect gap two-photon absorption. The quality of the results enabled us to test some of the theoretical predictions concerning these phenomena.

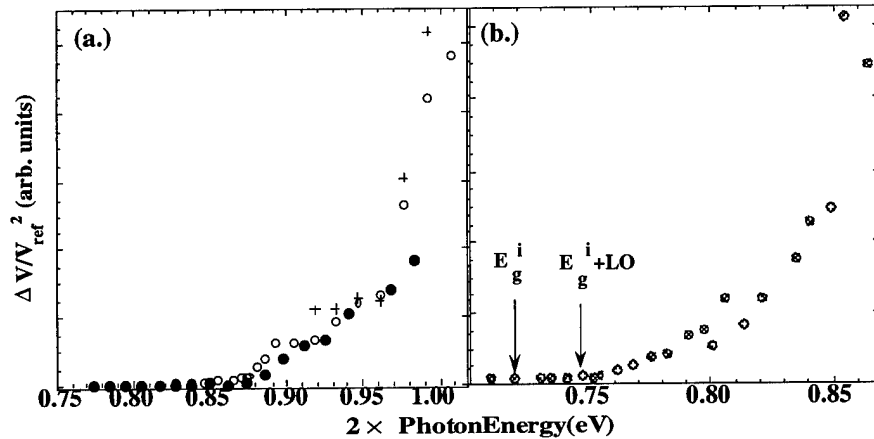


Fig. 2. Two-photon absorption in Ge at 125 K in the region near the indirect gap two-photon absorption. The two-photon photoconductivity signal is normalized to the square of the reference signal, V_{ref} , and plotted as a function of twice the FEL photon energy. The vertical arrows mark the indirect-gap, E_g^i , and the corresponding threshold for LO-phonon assisted processes as predicted by Bassani-Hassan theory.

For example, twenty years ago Bassani and Hassan had predicted a rather peculiar role of phonons in the indirect gap two-photon absorption, but such a prediction had never been tested. Our data clearly show that the prediction was correct. Two points should be emphasized concerning this background of practical achievements. First of all, the results determined our subsequent strategy in the development of the program. This is an important point, since our original proposal contained several research areas. No one of them failed: we simply decided to put our major effort in the areas that were already producing excellent results, and we fully intend to implement all of the parts of our original program. The strategy, however, will be the same: to exploit the successes to the limit. Second relevant point: the sustained record of successful FEL experiments on semiconductors removed a major question concerning our original proposal: in simple words, no one had ever tried to systematically rather than occasionally use an FEL for semiconductor materials research. Experience with other centralized facilities indicates that major unforeseen roadblocks can be encountered, which make it impossible to practically exploit an otherwise very promising facility. Our results show that such is not the case for the FEL. We have demonstrated, experiment after experiment, that the FEL can be used as a sophisticated but reliable instrument. Its record is already better than synchrotron radiation in its first decade of life, and much better than synchrotron radiation at its birth. There are no questions, therefore, about the suitability of the FEL for these experiments as well as for the other experiments that are part of the present proposal. We finally note that the use of a centralized facility always poses practical problems that must be eliminated with practical solutions. The successes of the program and the parallel funding by American and Swiss sources has made it possible for quite a few scientists to directly participate in these FEL experiments. We are *de facto* training the first specialized research team in the use of the FEL for materials studies. Our personnel are gaining extremely valuable hands-on experience in the use of the facility, which is absolutely required for the move to even more sophisticated experiments, and is a guarantee of their success. In essence, the first

successes of our program are both the background for many additional studies in the same lines of research, and the background for the new lines here proposed.

In addition to these advances, a large number FEL and FEL-related projects have been completed and are described in the following publications.

List of Publications

1. "The Vanderbilt Free-Electron Laser Center for Biomedical and Materials Research," by N. H. Tolk, C. A. Brau, G. S. Edwards, G. Margaritondo and J. T. McKinley. SPIE **1552**, 7, Short-Wavelength Radiation Sources (1991).
2. "Desorption Kinetics of Li-atom Delayed Emission from LiF Under Low-energy-electron Bombardment," by N. Seifert, D. Liu, R. G. Albridge, A. V. Barnes, N. Tolk, W. Husinsky and G. Betz. Phys. Rev. **B 46**, 83-89 (1992).
3. "Electron and Photon Stimulated Desorption as a Probe of the Dynamics of Molecules on Surfaces," by Jun Xu, A. V. Barnes and N. H. Tolk. J. Vac. Sci. Technol. **A 10**, 2216 (1992).
4. "Gas-exposure Enhanced Na* Emissions from Na-rich Surfaces," by Jun Xu, R. G. Albridge, A. V. Barnes, X. Yang and N. H. Tolk. Appl. Phys. Lett. **60**, 1396 (1992).
5. "Generation of Excited CN Electronically Emitted from Alkali-halide and Alkali-metal Surfaces," by Jun Xu, R. G. Albridge, A. V. Barnes, M. Riehl-Chudoba, A. Ueda, N. H. Tolk, D. Russell and P. Wang. Surf. Sci., **262**:77 (1992).
6. "Interface Measurements of Heterojunction Band Lineups with the Vanderbilt Free Electron Laser," by C. Coluzza, E. Tuncel, J.-L. Staehli, P. A. Baudat, G. Margaritondo, J. T. McKinley, A. Ueda, A. V. Barnes, R. G. Albridge, N. H. Tolk, D. Martin, F. Morier-Genoud, C. Dupuy, A. Rudra and M. Ilegems, Phys. Rev. **B 46**, 12834 (1992).
7. "Simultaneous Measurements of Transmission Optical Absorption and Electron Stimulated Li Desorption on LiF Crystals," by N. Seifert, H. Ye, D. Liu, R. Albridge, A. Barnes, N. Tolk, W. Husinsky and G. Betz, *Desorption Induced by Electronic Transitions (DIET V)* p. 309 (Springer Verlag, November 1992).
8. "New Mechanism for the Desorption of Excited Atoms by Photon Bombardment of Alkali Halide Crystals," by D. Liu, R. Albridge, A. Barnes, P. H. Bunton, C. S. Ewig, N. H. Tolk, M. Szymonski, *Desorption Induced by Electronic Transitions (DIET V)* p. 304 (Springer Verlag, November 1992).
9. "Rotational Distributions Following DIET: CN* from Alkali-Rich Surfaces", by J. Xu, L. Hulet, Jr, R. Albridge, A. Barnes, N. Tolk, *Desorption Induced by Electronic Transitions (DIET V)* p. 313 (Springer Verlag, November 1992).
10. "Simultaneous Measurements of Transmission Optical Absorption and Electron Stimulated Li Desorption on LiF Crystals," by N. Seifert, H. Ye, D. Liu, R.

Albridge, A. Barnes, N. Tolk, W. Husinsky and G. Betz, Nucl. Instr. Meth. in Phys. Res. **B 72**, 401-408 (1992).

11. "The Desorption of Excited Atoms by Photon bombardment of Alkali Halide Crystals," by D. Liu, R. G. Albridge, A.V. Barnes, P.H. Bunton, C.S. Ewig, N. H. Tolk and M. Szymonski, Surf. Sci. Lett. **281**, L353-L357 (1993).
12. "Simultaneous Laser-induced Fluorescence and Quadrupole Mass Spectroscopy Studies of Electron Stimulated Desorption of Ground State Lithium Atoms from Lithium Fluoride Crystals," by N. Seifert, D. Liu, A. Barnes, R. Albridge, Q. Yan, N. Tolk, W. Husinsky and G. Betz, Phys. Rev. **B 47**, 14 (1993).
13. "Free-Electron Laser Measurements of Direct and Phonon-Assisted Indirect Two-Photon Absorption in Germanium," by E. Tuncel, J. L. Staehli, C. Coluzza, G. Margaritondo, J. T. McKinley, R. G. Albridge, A. V. Barnes, A. Ueda, X. Yang and N. H. Tolk, Phys. Rev. Lett. **70**, 4146 (1993).
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15. "Excitation Spectroscopy of Thin-Film Disordered Semiconductors," by S.Q. Gu and P.C. Taylor, J. T. McKinley, A Ueda, X Yang and N. H. Tolk, (accepted for publication in Proceedings of SPIE, Los Angeles, CA, January 21-25, 1993).
16. "Semiconductor Spectroscopy and Ablation Processes with the Vanderbilt FEL," by N. H. Tolk, R. G. Albridge, A. V. Barnes, J. T. McKinley, A. Ueda, J. F. Smith, J. L. Davidson, M. L. Languell, C. Coluzza, E. Tuncel, and G. Margaritondo. (accepted for publication in Proceedings of SPIE, Los Angeles, CA, January 21-25, 1993).
17. "Electronically Induced Sputtering of Ground and Excited State Alkali Atoms from Alkali Halide Crystals," by N. Seifert, H. Ye, D. Liu, R. Albridge, A. Barnes, N. Tolk, W. Husinsky and G. Betz, Proceedings of *Ninth International Workshop on Inelastic Ion Surface Collisions (IISC-9)*, Aussois, France, Fall 1992.
18. "Photon- and Electron-Stimulated Desorption of Excited Alkali-metal Atoms from Alkali Halides," by D. Liu, N. Seifert, D. J. McClure, A. V. Barnes, R. G. Albridge, N. H. Tolk, and D. Russell, Phys. Rev. **B 47**, 1553 (1993).
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21. "Tunable Laser Desorption from Diamond Films and Pyrolytic Graphite," by A. Ueda, J. T. McKinley, R. G. Albridge, A. V. Barnes, N. H. Tolk, J.L. Davidson and M. L. Languell, *Mat. Res Soc. Symp. Proc.* **285** 215 (1993).
22. "Wavelength-Dependent Laser Ablation of Diamond Films," by J. T. McKinley, A. Ueda, R. G. Albridge, A. V. Barnes, N. H. Tolk, J.L. Davidson and M. L. Languell, *E Proc. of 2nd Intl. Conf. on Laser Ablation*, Knoxville, 1993.